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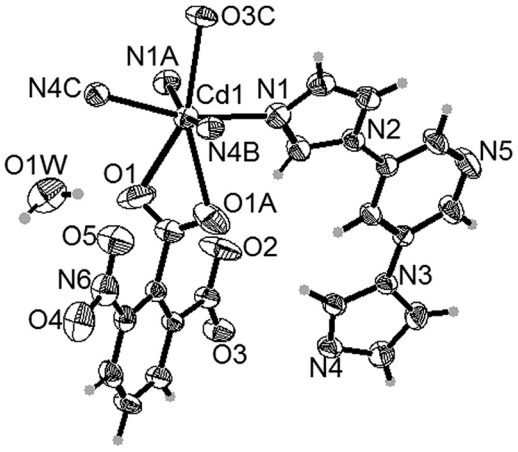
Crystal structure of *catena*-poly[bis(μ_2-3,5-bis(1-imidazolyl)pyridine-κ^2*N*:*N*′)-(μ_2-3-nitrophthalato-k^3*O*,*O*′:*O*″)cadmium(II)] dihydrate, $C_{30}H_{25}N_{11}O_8Cd$



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Abstract

$C_{30}H_{25}N_{11}O_8Cd$, orthorhombic, *Pnma* (no. 62), a = 17.9344(3) Å, b = 18.2722(3) Å, c = 9.5619(2) Å, V = 3133.44(10) Å^3, Z = 4, $R_{gt}(F)$ = 0.0345, $wR_{ref}(F^2)$ = 0.0707, T = 293.28(10) K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.39 × 0.35 × 0.29 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	0.77 mm^{-1}
Diffractometer, scan mode:	SuperNova, ω
θ_{max}, completeness:	28.4°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	35240, 3786, 0.038
Criterion for I_{obs}, $N(hkl)_{gt}$:	I_{obs} > 2 σ(I_{obs}), 3390
$N(param)_{refined}$:	266
Programs:	Bruker [1], Olex2 [2], SHELX [3, 4]

Source of material

All chemical reagents were used without further purification. The 3-nitrobenzene-1,2-dicarboxylic acid were purchased from Beijing Bailingwei Technology Co., Ltd. 3,5–Bis(1-imidazolyl)pyridine was bought from Jinan Henghua Technology Co., Ltd. All other chemical reagents were of analytical grade and obtained from the Tianjin Deen Chemical Reagent Co., Ltd. The mixture of 3-nitrobenzene-1,2-dicarboxylic acid ($H_2$3–Nbdc 21.4 mg, 0.1 mmol), 3,5-bis(1-imidazolyl)pyridine (bip, 21.1 mg, 0.1 mmol), $Cd(OAc)_2{\cdot}2H_2O$ (26.7 mg, 0.1 mmol), NaOH (4 mg, 0.10 mmol) and H_2O (6 mL) was placed in a 23 ml Teflon-lined autoclave at 393 K for four days, then cooled to room temperature. Colorless block crystals were obtained in ca. 62% yield. **Elemental analysis** calcd. (%) for $C_{30}H_{25}N_{11}O_8Cd$: C, 46.20; H, 3.23; N, 19.75 Found: C, 46.24; H, 3.28; N, 19.68.

Experimental details

Using Olex2 [2]. The structure was solved with the SheLXT [3] structure solution program using Intrinsic Phasing and refined with the ShelXL [4] refinement package. Hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms. The U_{iso} of the H-atoms were constrained to 1.2 times U_{eq} of their bonding carbon atoms with C–H = 0.93 Å (aromatic) and 1.5 times U_{eq} for the hydrogen atoms at water with

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Cd1	0.77972 (2)	0.2500	0.66270 (2)	0.03121 (8)
O1	0.65926 (11)	0.19115 (13)	0.5787 (2)	0.0705 (6)
O2	0.53199 (14)	0.2500	0.7699 (3)	0.0689 (10)
O3	0.41098 (12)	0.2500	0.7344 (2)	0.0446 (6)
O4[a]	0.617 (2)	0.2500	0.1207 (9)	0.063 (6)
O4A[b]	0.6354 (13)	0.2370 (12)	0.1218 (8)	0.049 (4)
O5[a]	0.6902 (5)	0.2500	0.3096 (12)	0.063 (8)
O5A[b]	0.6798 (11)	0.2888 (15)	0.3005 (12)	0.062 (4)
N1	0.75623 (11)	0.33807 (11)	0.8313 (2)	0.0376 (5)
N2	0.68961 (10)	0.40227 (10)	0.98075 (19)	0.0321 (4)
N3	0.42468 (9)	0.40188 (10)	1.07742 (19)	0.0308 (4)
N4	0.33385 (10)	0.33930 (11)	0.9786 (2)	0.0365 (4)
N5	0.58255 (12)	0.47644 (15)	1.2737 (3)	0.0609 (7)
N6	0.6294 (2)	0.2500	0.2458 (3)	0.0487 (8)
C1	0.62986 (18)	0.2500	0.5504 (3)	0.0392 (8)
C2	0.55712 (16)	0.2500	0.4701 (3)	0.0272 (6)
C3	0.48730 (16)	0.2500	0.5341 (3)	0.0273 (6)
C4	0.42285 (19)	0.2500	0.4531 (4)	0.0370 (7)
H4	0.3766	0.2500	0.4970	0.044*
C5	0.4263 (2)	0.2500	0.3078 (4)	0.0446 (9)
H5	0.3828	0.2500	0.2550	0.054*
C6	0.4940 (2)	0.2500	0.2436 (3)	0.0407 (8)
H6	0.4971	0.2500	0.1465	0.049*
C7	0.55819 (19)	0.2500	0.3238 (3)	0.0330 (7)
C8	0.47659 (17)	0.2500	0.6933 (3)	0.0321 (7)
C9	0.80166 (12)	0.38767 (14)	0.8971 (3)	0.0390 (6)
H9	0.8525	0.3930	0.8805	0.047*
C10	0.68976 (13)	0.34834 (14)	0.8837 (2)	0.0366 (5)
H10	0.6477	0.3219	0.8575	0.044*
C11	0.76203 (12)	0.42761 (14)	0.9893 (3)	0.0406 (6)
H11	0.7798	0.4647	1.0469	0.049*
C12	0.62803 (11)	0.42313 (12)	1.0641 (2)	0.0304 (5)
C13	0.55656 (11)	0.40576 (12)	1.0234 (2)	0.0314 (5)
H13	0.5477	0.3831	0.9378	0.038*
C14	0.49865 (11)	0.42256 (12)	1.1117 (2)	0.0298 (5)
C15	0.51346 (14)	0.45809 (15)	1.2361 (3)	0.0486 (7)
H15	0.4741	0.4696	1.2954	0.058*
C16	0.63851 (13)	0.45907 (16)	1.1889 (3)	0.0483 (7)
H16	0.6868	0.4717	1.2150	0.058*
C17	0.40561 (12)	0.35089 (13)	0.9806 (2)	0.0336 (5)
H17	0.4396	0.3271	0.9228	0.040*
C18	0.30452 (13)	0.38498 (15)	1.0785 (3)	0.0449 (6)
H18	0.2541	0.3888	1.0999	0.054*
C19	0.35921 (13)	0.42348 (15)	1.1409 (3)	0.0430 (6)
H19	0.3539	0.4577	1.2123	0.052*
O1W	0.61506 (12)	0.04498 (13)	0.5852 (2)	0.0720 (6)
H1WA	0.6273	0.0899	0.5972	0.108*
H1WB	0.6014	0.0360	0.5018	0.108*

[a]Occupancy: 0.44(6), [b]Occupancy: 0.28(3).

O–H = 0.85 Å. The O4 and O5 atoms were disordered and the components of disordered atoms were refined isotropically.

Comment

Metal-organic Complexes have always been in the spotlight for a long time not only for their diversities of structures [5–8], but also for their strong thermal and chemical stabilities [9–12]. At the same time, they have attractive application prospects in many fields such as gas storage/separations, fluorescent sensing, nonlinear optics, magnetic, catalysis, and so on [13–16]. Carboxylate ligands with the electron-withdrawing group ($-NO_2$) are widely used as an oxygen-donor ligand because the N and O atoms in the $-NO_2$ group can not only serve as coordination sites but also as acceptors for hydrogen-bonds to enrich the structural and functional diversities of coordination polymers [16]. In our previous work, we had synthesized a series of metal-organic compounds with diverse structures and excellent properties such as magnetism, fluorescent, photochemical and photocatalytic properties based on 3-nitrophthalic acid [17–19] and 4-nitrophthalic acid [16, 20–22]. Among the N-donor ligands, the imidazolyl ligands are the most common N-donor ligands to combine with O-donor ligands to adjust the structures and properties of metal-organic complexes [23]. The 3,5-bis(1-imidazolyl)pyridine (bip) is one of many imidazolyl N-donor ligands which were used to synthesize metal-organic complexes [24–27]. In this study, we selected the 3-nitrobenzene-1,2-dicarboxylic acid ($H_2$3–Nbdc) as an educt, 3,5-bis(1-imidazolyl)pyridine (bip) as a N-donor ligand, cadmium acetate as Cd-metal supplier to obtain the coordination polymer.

The single-crystal X-ray analysis shows that the title complex crystallizes in orthorhombic crystal system and features a one-dimensional chain. The asymmetric unit contains a half Cd(II) ion, a half 3–Nbdc dianion, one bip molecule, and one guest water molecule, as shown in the figure (A: x, $0.5 - y$, z; B: $0.5 + x$, y, $1.5 - z$; C: $0.5 + x$, $0.5 - y$, $1.5 - z$). The Cd(II) ion is seven coordinated by three oxygen atoms and four nitrogen atoms. Among them, three oxygen atoms are from two symmetry-related 3–Nbdc dianions, and the other four nitrogen atoms are from three symmetry-related bip ligands. The seven-coordinated Cd(II) ion forms a slightly distorted single cap octahedral [CoN_4O_3] geometry with the four atoms (N1, N1A, N4B, N4C) in the equatorial plane and the other three atoms (O1, O1A, O3B) in the axial position (see the Figure). The Cd–O bond lengths are 2.551(2) and 2.543(2) Å, whilst the Cd–N bond lengths are 2.317(2) and 2.3304(19) Å, respectively. The bond angles around the Cd centers range from 50.02(10) to 164.94(7)°.

The two carboxyl groups of one 3–Nbdc anion adopt chelating-bidentate and monodentate coordination modes, respectively. Every two cadmium atoms are linked together

through one 3–Nbdc dianion and two bip molecules by an external single bridging coordination mode to form a chain with the Cd···Cd distance of 9.1213(1) Å. Adjacent chains are linked through hydrogen bonds between free water oxygen atom and nitrogen atom from bip molecules (O(1W)–H(1WB)···N5: d = 2.22 Å) along the c direction to generate a two-dimensional layer with the nearest Cd···Cd separation of 9.5619(2) Å. The adjacent layers stack together in a –*ABAB*-sequence to achieve a whole three-dimensional supramolecular structure *via* very weak interlayer π-π interactions between pyridine ring and imidazole ring of bip ligands. The centroid-centroid distance and the dihedral angle between pyridine ring and imidazole ring are 3.9677(0) Å and 15.9°, respectively.

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References

1. Rigaku Inc., CrysAlis^{PRO} Tokyo, Japan (2015).
2. Dolomanov O. V., Bourhis L. J., Gildea R. J., Howard J. A. K., Puschmann H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* 2009, *42*, 339–341.
3. Sheldrick G. M. SHELXTL – integrated space-group and crystal-structure determination. *Acta Crystallogr.* 2015, *A71*, 3–8.
4. Sheldrick G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr.* 2015, *C71*, 3–8.
5. Yue Y. F., Qian G. D., Chen B. L. Luminescent functional metal-organic frameworks. *Chem. Rev.* 2012, *112*, 1126–1162.
6. Xuan W. M., Zhu C. F., Liu Y., Cui Y. Mesoporous metal-organic framework materials. *Chem. Soc. Rev.* 2012, *41*, 1677–1695.
7. Pan J., Zhang D., Xue Z. Z., Wei L., Han S. D., Wang G. M. Three d_{10} coordination polymers assembled from 3,5-bis(imidazole-1-yl) pyridine and different polycarboxylates: syntheses, structures and luminescence properties. *Solid State Sci.* 2017, *73*, 13–18.
8. Wang Y. F., Zhang Y. H. A new 3D Cd(II) coordination polymer constructed by mixed-ligand strategy: synthesis, crystal structure and properties. *Inorg. Nano–Mat. Chem.* 2021, *51*, 303–308.
9. Chang X. H., Zhao Y., Feng X., Ma L. F., Wang L. Y. Syntheses, structures and fluorescent properties of cadmium coordination polymers based on 2,3′,5,5′-biphenyl tetracarboxylate and N-donor ancillary ligands. *Polyhedron* 2014, *83*, 159–166.
10. Ju F. Y., Li Y. P., Li G. L., Liu G. Z., Xin L. Y., Li X. L. Zinc(II) and cadmium(II) coordination polymers with various polynuclears spaced by semirigid 4-carboxybenzeneacetate and nitrogen-rich co-ligands: syntheses, structures and properties. *Chin. J. Inorg. Chem.* 2016, *32*, 1876–1884.
11. Yin W. D., Li G. L., Li X. L., Xin L. Y., Ma L. F., Liu G. Z. Syntheses, structures and fluorescent properties of two zinc coordination polymers based on the itaconic acid. *Chin. J. Inorg. Chem.* 2016, *32*, 662–668.
12. Yin W. D., Li G. L., Xin L. Y., Li X. L., Ma L. F., Liu G. Z. Solvothermal syntheses, crystal structures, and luminescent properties of three coordination polymers derived from semirigid 3-(carboxymethyl) benzonic acid and dipyridyl coligands. *Chin. J. Struct. Chem.* 2017, *36*, 1502–1510.
13. Zhao Y., Wang L., Fan N. N., Han M. L., Yang G. P., Ma L. F. Porous Zn(II)-based metal-organic frameworks decorated with carboxylate groups exhibiting high gas adsorption and separation of organic dyes. *Cryst. Growth Des.* 2018, *47*, 7114–7121.
14. Liu G. Z., Li S. H., Li X. L., Xin L. Y., Wang L. Y. Three series of MOFs featuring various metal(II)-carboxylate chains cross-linked by dipyridyl-typed coligands: synthesis, structure, and solvent-dependent luminescence. *CrystEngComm* 2013, *15*, 4571–4580.
15. Xue L. P., Li Z. H., Zhang T., Cui J. J., Gao Y., Yao J. X. Construction of two Zn(II)/Cd(II) multifunctional coordination polymers with mixed ligands for catalytic and sensing properties. *New J. Chem.* 2018, *42*, 14203–14209.
16. Li G. L., Yin W. D., Liu G. Z., Ma L. F., Wang L. Y. Syntheses, structures and magnetic properties of four coordination polymers based on nitrobenzene dicarboxylate and various N-donor coligands. *J. Solid State Chem.* 2014, *220*, 1–8.
17. Li G. L., Liu G. Z., Xin L. Y., Li X. L., Ma L. F., Wang L. Y. Syntheses, structures and fluorescence properties of four Zn/Cd(II) coordiation polymers with 3-nitrobenzene-1,2-dicarboxylate and dipyridyl-typed coligands. *J. Inorg. Organomet. Polym.* 2015, *25*, 694–701.
18. Yin W. D., Li G. L., Liu G. Z., Xin L. Y., Li X. L., Ma L. F. Syntheses, structures and properties of two coordination polymers constructed by 3-nitrobenzene-1,2-dicarboxylate acid and Zn/Co. *Chin. J. Inorg. Chem.* 2015, *31*, 1439–1446.
19. Yin W. D., Liu Q. L., Li G. L. Crystal structure of *catena*-poly [triaqua-(1,3-di(1H-imidazol-1- yl)benzene-κ^2*N*:*N*′)-(3-nitrophthalato-κ^1*O*)cobalt(II)]-water (2/3), $C_{20}H_{22}N_5O_{10.5}Co$. *Z. Kristallogr. N. Cryst. Struct.* 2020, *235*, 125–128.
20. Li G. L., Liu G. Z., Huang L. L., Li L., Zhang X. Ancillary ligand-mediated syntheses, structures and fluorescence of three Zn/Cd(II) coordination polymers based on nitrobenzene dicarboxylate. *J. Inorg. Organomet. Polym.* 2014, *24*, 617–623.
21. Li G. L., Liu G. Z., Ma L. F., Xin L. Y., Li X. L., Wang L. Y. Crystallographic determination of solid-state structural transformations in a dynamic metal-organic framework. *Chem. Commun.* 2014, *50*, 2615–2617.
22. Li G. L., Liu G. Z., Xin L. Y., Li X. L. Two new coordination polymers containing metal-carboxylate helix. *Chin. J. Struct. Chem.* 2014, *33*, 764–770.
23. Xin L. Y., Liu G. Z., Ma L. F., Zhang X., Wang L. Y. Structural diversity and fluorescence regulation of three Zn_{II} coordination polymers assembled from mixed ligands tectons. *Aust. J. Chem.* 2015, *68*, 758–765.
24. Zhao C. J., Zhao L., Zhang M. Syntheses, characterizations and luminescence properties of four novel coordination polymers based on 4,4′-(phenylazanediyl)dibenzoic acid with two rigid N-donor imidazol ligand. *Inorg. Chim. Acta* 2018, *469*, 136–143.
25. Zhang H., Zhu Z. Q., Zhou F. H., Redshaw C., Chen K., Xu J. Two dimensional coordination polymers based on 3,5-di(1*H*-imidazol-1-yl) pyridine and their fluorescence properties. *J. Mol. Struct.* 2020, *1207*, 127818.

26. Yuan F., Yuan C. M., Zhou C. S., Qiao C. F., Lu L., Ma A. Q., Singh A., Kumar A. Syntheses and photocatalytic properties of three new d_{10}-based coordination polymers: effects of metal centres and ancillary ligands. *CrystEngComm* 2019, *21*, 6558–6565.

27. Wei-Wei L., Feng-Yang J. Crystal structure of catena-poly[aqua-(μ_2 -(3,5-di(1*H*-imidazol-1-yl)-pyridine-κ^2N:N′)-(μ2-2-(carboxylatomethyl)benzoato-κ^2O:O′)] cadmium(II), $C_{20}H_{17}CdN_5O_5$. *Z. Kristallogr. N. Cryst. Struct.* 2018, *233*, 545–546.